

Atomic Layer Etching

Room Hall 3F - Session ALE1-WeM

Plasma and Energy-Enhanced ALE

Moderators: Dr. Dmitri Kioussis, Intel Corporation, Prof. Christophe Vallée, University of Albany

8:00am **ALE1-WeM-1 Anisotropic and Isotropic Plasma-Enhanced Atomic Layer Etching Processes for Metals and Dielectric Materials for Semiconductor Devices, Heeyeop Chae**, Sungkyunkwan University (SKKU), Republic of Korea

INVITED

The critical dimensions of semiconductor devices are continuously shrinking with 3D device structure and are approaching to nanometer scale. The demand for dimension control in angstrom level is drastically increasing also in etching processes. In this talk, various plasma-enhanced ALE (PEALE) processes are discussed for anisotropic and isotropic patterning of metals and dielectric materials including molybdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, aluminum oxide, hafnium oxide, zirconium oxides, silicon oxide, and silicon nitride. [1-10] Typical ALE processes consist of surface modification step and removal step. Various surface modification schemes were applied including fluorocarbon deposition on surface, surface fluorination, surface chlorination, surface oxidation with radicals generated with plasmas. For the removal or etching step, the modified layers were removed by ion-bombardment, heating, ligand exchange, ligand volatilization, or halogenation. The characteristics of reaction kinetics, surface roughness, surface residue in the plasma-enhanced ALE processes will be also discussed.

- 1) K. Koh, Y. Kim, C.-K. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 36(1), 10B106 (2017)
- 2) Y. Cho, Y. Kim, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022604 (2020)
- 3) Y. Kim, S. Lee, Y. Cho, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022606 (2020)
- 4) D. Shim, J. Kim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. B.*, 40(2) 022208 (2022)
- 5) Y. Lee, Y. Kim, J. Son, H. Chae, *J. Vac. Sci. Technol. A.*, 40(2) 022602 (2022)
- 6) J. Kim, D. Shim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. A.*, 40(3) 032603 (2022)
- 7) Y. Kim, S. Chae, H. Ha, H. Lee, S. Lee, H. Chae, *Appl. Surf. Sci.* 619, 156751 (2023)
- 8) Y. Kim, H. Kang, H. Ha, C. Kim, S. Cho, H. Chae, *Appl. Surf. Sci.* 627, 157309 (2023)
- 9) Y. Kim, H. Kang, C. Kim, H. Chae, *ACS Sustain. Chem. Eng.* 11(16), 6136 (2023)
- 10) Y. Kim, H. Kang, H. Ha, M. Choi, M. Jeon, S. Cho, H. Chae, *Plasma Process. Polym.*, DOI: 10.1002/ppap.202300161, (2023)

8:30am **ALE1-WeM-3 Plasma Atomic Layer Etching of Titanium Nitride with Surface Fluorination or Chlorination and Ar Ion Bombardment, Heeju Ha**, H. Lee, M. Jeon, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

Plasma atomic layer etching (ALE) processes were developed for titanium nitride (TiN) with surface fluorination or chlorination in the modification step and ion bombardment in the removal step. In the modification step, the TiN surface was fluorinated using NF_3 plasma to form Ti-F bonds or chlorinated using BCl_3 plasma to form Ti-Cl bonds. The fluorinated or chlorinated layers were removed by ion bombardment using Ar plasma. The etch per cycle (EPC) of TiN was investigated depending on ion energy and etching time. The ALE window of constant EPC of TiN was confirmed in the energy range of 25 – 80 V for fluorination and 70 – 80 V for chlorination. The EPC of TiN was determined to be 1.5 nm/cycle in fluorination and 3.8 nm/cycle in chlorination in the ALE window region. The EPC of TiN increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for both fluorination and chlorination. The strong Ti-F peak was observed about 13% on the surface after ALE process with fluorination, but small Ti-Cl peaks were observed below 1% after ALE process with chlorination. The Root-mean-square (RMS) roughness of the TiN surface after ALE was measured at 0.24 nm for fluorination and 0.29 nm for chlorination, which is lower than before etching.

8:45am **ALE1-WeM-4 Isotropic Plasma Atomic Layer Etching of Nickel Aluminide Binary Intermetallic Using a Super-Cycle Sequence Based on Hf and Al(CH₃)₃, Ali Mohamed Ali**, IMEC Belgium; G. Krieger, TU / Eindhoven, Netherlands; J. Soulié, C. Pashartis, IMEC Belgium; C. Detavernier, Ghent University, Belgium; H. C. M. Knoops, E. Kessels, TU / Eindhoven, Netherlands; S. De-Gendt, F. Lazzarino, S. Kundu, J. de Marneffe, IMEC Belgium

Nickel aluminides have attracted tremendous research attention as a potential alternative material for barrier-less interconnects and EUV mask absorber applications due to its lower resistivity than other elemental metals and higher printing resolution, respectively.^{1,2} However, down-scaling these binary intermetallics brings emerging challenges in developing etch methods due to the high chemical inertness and low gas-phase volatility of Ni compounds. In addition, preserving the concentration of each element in the alloy during the etching process is essential to be useable at the nanoscale. In this work, we report a new and promising approach towards the atomic layer etching (ALE) of stoichiometric NiAl and Ni₃Al. A super-cycle ALE process has been developed, in which each sub-cycle enables the removal of the Al-rich and Ni-rich phases, respectively. Fluorine-containing plasma and trimethyl-aluminum (TMA) precursors have been utilized to etch Al in the first phase. Whereas, in the second phase, the etching of Ni has been achieved using a nitrogen-containing plasma, probably forming Ni nitride and then chelation by hexafluoro-acetylacetone (Hf ac) precursor. A fundamental ALE study on each individual ALE process has been performed on pure Ni and pure Al films to evaluate the etching efficiency and selectivity of each element versus the other. *In-situ* spectroscopic ellipsometry measurements were employed to elucidate the self-limiting nature of the ALE sequence on the pure metal film and thickness change during alloy etching. The saturation behavior for each precursor on the compatible pure metal films has been observed. X-ray reflectivity measurements were carried out to confirm the etch rates on Ni-aluminide films. The etch rates were varied from $0.5 \pm 0.10 \text{ \AA/super-cycle}$ at 250 °C to $3.3 \pm 0.23 \text{ \AA/super-cycle}$ at 350 °C. Furthermore, atomic force microscopy analysis shows that thin Ni aluminide films remained smooth during initial etching and might introduce a little roughness when the etch cycles progressed. The results obtained from x-ray photoelectron spectroscopy confirmed that, at the optimized super-cycle ALE process, the etched Ni aluminide films still preserve the same concentration of each element in the alloy. The developed ALE process enabled the etching of nickel aluminide alloys and created a paradigm for future studies on alternative etching of binary intermetallics.

[1] Soulié, Jean-Philippe, et al. "Reduced resistivity of NiAl by back thinning for advanced interconnect metallization." IEEE, 2023.

[2] Luong, Vu, et al. "Ni-Al alloys as alternative EUV mask absorber." Applied Sciences 8.4(2018):521.

9:00am **ALE1-WeM-5 Surface Effects in Quasi-ALE of Si: A Correlation with Ar⁺ Ion Energy, O. Danielsson**, Lund University, Sweden; A. Karimi, M. Asif, AlixLabs AB, Sweden; S. Khan, Danish Fundamental Metrology Institute, Denmark; Ivan Maximov, Lund University, Sweden

Atomic Layer Etching (ALE) is a self-limiting process used in nanofabrication that allows for precise material removal on the atomic scale by a cyclic nature introducing reactive gas adsorption and removal of surface atoms by a low-energy ion bombardment. In practical realisation of ALE, e.g. using commercially available RIE tools, the ion energy in plasma may exceed the sputtering threshold, typically 20-40 eV. It will result in a quasi-ALE (Q-ALE) regime where the process steps are not self-limiting, but still highly accurate and of lower damage compared to RIE. Direct measurements of the ion energy in Q-ALE are thus instrumental for studies of both the etching process and surface damage effects.

For Si etching experiments, we have used a commercial Inductively Coupled Plasma RIE Takachi™ tool from Plasma-Therm LLC, USA. The tool operates in a Cl₂-molecular activation regime using Ar RF-plasma to desorb the etch reaction products in the etch step. Unpatterned silicon-on-insulator (SOI) 10x10 mm² samples with a 50 nm thick top Si layer were used for the etching experiments and characterised by spectroscopic ellipsometry and AFM. Typically, the Q-ALE operated in a 25 cycle mode, sufficient to measure the Si thickness difference by ellipsometry using a 4-layer model. A Retarding Field Energy Analyzer (RFEA) from Impedance LLC, Ireland, was installed to measure the Ar⁺ ion energy and ion current densities at different Q-ALE conditions, such as RF-power and pressure. The surface effects of the etched SOI samples are characterised by AFM, SEM and Kelvin Probe Force Microscopy (KPFM).

Wednesday Morning, August 7, 2024

In this work we present the actual data of Ar⁺ ion energy distribution and the ion current densities at the sample level in the commercial Takachi™ RIE tool operating in Q-ALE mode. In order to reach a low ion energy regime, we used RF-power in the range of 3-16 W, that corresponds to the bias voltages of 10-120 V. In this voltage range the ion energy peak shifts from ≈50 to 147 eV, respectively, with an increase in the RF-power. The calculated Ar⁺ ion flux from the measured ion currents is about $3 \times 10^{13} - 2 \times 10^{14}$ ion cm⁻² s⁻¹ that fits well with the published data. Etch per cycle (EPC) was measured in both sputtering (no Cl₂) and ALE-regime at different bias set-points (RF-power). A clear EPC plateau for the ALE regime was observed at biases of 20-40 V that corresponds to the peak Ar⁺ ion energy of 50-70 eV. The AFM and high-resolution SEM data demonstrated a decreased surface roughness of etched Si in the plateau region indicating a low surface damage. More details to be presented.

9:15am **ALE1-WeM-6 Atomic Layer Etching Study of Polycrystalline, Epitaxial and Doped ZnO Films Using *in Situ* Spectroscopic Ellipsometry**, **Terrick McNealy-James**, N. Berriel, B. Butkus, T. Currie, T. Jurca, P. Banerjee, University of Central Florida

Atomic layer etching (ALE) offers sub-nm level control over film removal, with two distinct categories: ion-driven anisotropic etching and thermal isotropic etching. Both options present a promising solution to address patterning challenges in device manufacturing. These mechanisms become particularly important when the extended atomic structure of films such as crystal facets, grain boundaries, and dopants are taken into consideration.

In this work, we study the ALE of a model film - zinc oxide (ZnO), with particular emphasis on observing the role of crystallinity and doping in determining film etch rates. We employ *in situ* spectroscopic ellipsometry as our tool of choice and comprehensively map the etch rate as a function of temperature and co-reactant pulse times. The resulting 3D contour plot of etch rate vs. temperature and time depicts the process parameter window. Importantly, the plot is visually appealing and can yield insightful information pertaining to ALE processes, in general.

The ALE chemistry¹ employed to etch ZnO consists of alternate pulses of acetylacetone and O₂ plasma while the temperature is varied from 100 °C to 300 °C. The etch rates of single crystalline (*e.g.*, c-axis oriented) films are compared with polycrystalline ZnO. The effect of dopants, such as Al³⁺ and Ti⁴⁺, on the etch rates of ZnO films are explored. The impact of ALE chemistry in determining etch rates in films with extended atomic structure such as crystal facets, grain boundaries and dopants are discussed with implications to future device manufacturing.

References:

(1) A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M. Kessels, and F. Roozeboom, ACS Appl. Mater. Interfaces, vol. 10, 38588, (2018).

9:30am **ALE1-WeM-7 Atomic Layer Etching of Diamond for Epitaxy Preparation**, **Julian Michaels**, University of Illinois at Urbana-Champaign; N. Deegan, Argonne National Laboratory, USA; Y. Taturyan, University of Chicago; J. Renzas, Oxford Instruments Plasma Technology; D. Awschalom, University of Chicago; J. Eden, University of Illinois at Urbana-Champaign, USA; F. Heremans, Argonne National Laboratory, USA

Renowned for its exceptional hardness and chemical impermeability, diamond is a wide bandgap semiconductor material with promising applications in optoelectronics, quantum optics, and beyond. Despite its desirable properties, the inherent manufacturing and fabrication challenges associated with monocrystalline diamond make it difficult to smooth, leading to lossy devices in its various applications. Moreover, existing methods for surface smoothing are often costly and time intensive.

In this context, atomic layer etching (ALE) emerges as a potentially viable solution for smoothing diamond surfaces. ALE is a cyclical process that precisely defines nanostructures by removing individual atomic layers. Recently, bias-pulsed ALE (BP-ALE), which is an augmented ALE process wherein reagent gases are not purged between steps, was shown to drastically smooth the surface of 4H-SiC substrates.

Here, we present a novel BP-ALE recipe tailored for diamond substrates. This innovative approach not only achieves precise etching of diamond but also facilitates rapid surface smoothing compared to existing conventional methods. To evaluate the efficacy of BP-ALE, diamond films were grown on etched surfaces, conventionally smoothed substrates, and commercially purchased substrates. Our findings indicate that BP-ALE not only expedites

surface smoothing but also yields growth-ready surfaces suitable for subsequent diamond growth.

In summary, our study underscores the potential of BP-ALE as a cost-effective and efficient method for smoothing diamond surfaces, thereby enhancing their suitability for various optoelectronic and quantum optical applications.

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